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(54) Title: OLEOYL SARCOSINATE CONTAINING DETERGENT COMPOSITIONS (57) Abstract Detergent compositions are provided which are especially effective for removing greasy/oily soils and stains from substrates such as fabrics or dishware during cleaning operations. Such compositions essentially contain a surfactant component comprising oleoyl sarcosinate and a water-soluble source of calcium and/or magnesium ions. Methods for washing these substrates and methods for pretreating these substrates using these compositions are also disclosed.		

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OLEOYL SARCOSINATE-CONTAINING DETERGENT COMPOSITIONS

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FIELD OF THE INVENTION

The present invention relates to detergent compositions and cleaning methods which employ oleoyl sarcosinate surfactant and a source of calcium and/or magnesium ions to enhance the removal of greasy or oily stains and soils from substrates.

BACKGROUND OF THE INVENTION

Most conventional detergent compositions contain mixtures of various
15 detergent surfactants in order to remove a wide variety of soils and stains from surfaces. For example, various anionic surfactants, especially the alkyl benzene sulfonates, are useful for removing particulate soils, and various nonionic surfactants, such as the alkyl ethoxylates and alkylphenol ethoxylates, are useful for removing greasy soils.

20 Oleoyl sarcosinate is a known anionic surfactant which has been used as the detergent surfactant, for example, in fabric laundering compositions. Oleoyl sarcosinate has been described in the following patents and publications: U.S. 2,542,385; U.S. 3,402,990; U.S. 3,639,568; U.S. 4,772,424; U.S. 5,186,855; European Patent Publication 505,129; British Patent Publication 1,211,545; Japanese
25 Patent Publication 59/232194; Japanese Patent Publication 62/295997; Japanese Patent Publication 02/180811; and Chemical Abstracts Service Abstracts Nos. 61:3244q, 70:58865x, and 83:181020p. Oleoyl sarcosinates are not known to be especially or particularly useful for removing greasy or oily stains or soil from substrates washed therewith.

30 It is also known that non-surfactant components of detergent compositions can affect the detergent performance of such compositions. For example, the presence of certain metal ions such as calcium and/or magnesium cations, whether added purposely to detergent compositions or present incidentally through the use of hard water, can affect sudsing and/or the stain/soil removal performance of detergent
35 compositions. For example, Ofosu-Asante/Willman/Foley, WO 93-05132; Published May 18, 1993 discloses that addition of calcium ions to certain types of detergent compositions can enhance the ability of such compositions to remove greasy and oily

stains from substrates washed therewith. Further, Venegas; U.S. 5,030,378; Issued July 9, 1991 discloses that addition of calcium ions to certain enzyme-containing detergent compositions can improve the stain and soil removal performance thereof.

Notwithstanding the prior art efforts to provide improved detergent compositions by selection of certain combinations of surfactants and other composition components, there is a continuing need to develop detergent compositions that may be especially effective for removing certain types of problematic soils or stains, e.g. oil or grease, from fabrics, dishware or other substrates to be cleaned using such compositions. It is, accordingly, an object of the present invention to provide detergent compositions, and methods for using them, which exhibit enhanced greasy and oily stain and soil removal performance. The compositions also provide excellent color care for dyed fabrics and excellent skin mildness for handwash operations. These and other advantages of the present invention will be seen from the disclosures hereinafter.

SUMMARY OF THE INVENTION

The present invention relates to detergent compositions which may be in the form of liquid, granular or gel products suitable for removing greasy or oily stains or soils from substrates including fabrics, dishware, and the like. Such compositions comprise at least about 1% of a deterative surfactant component which comprises an oleoyl sarcosinate surfactant and at least 0.05% of a water-soluble source of calcium and/or magnesium ions.

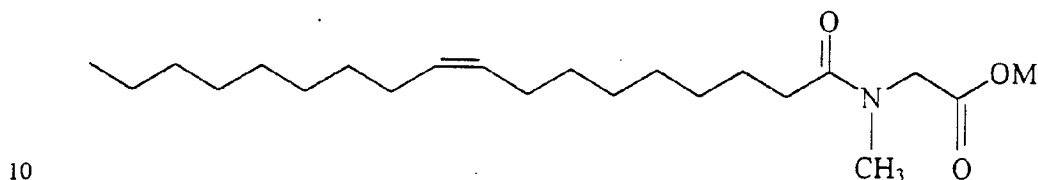
The present invention also relates to a method for cleaning substrates soiled with greasy and/or oily soils. Such a method comprises contacting such soiled substrates with an aqueous solution containing from about 500 to 10000 ppm of a detergent composition as hereinbefore described. In another embodiment, such a method comprises pretreating greasy/oily stains or soils on substrates by contacting such stains or soils with highly concentrated forms of such detergent compositions. This contact should occur prior to the conventional washing of such substrates in aqueous wash solution.

DETAILED DESCRIPTION OF THE INVENTION

The components of the detergent compositions herein, their preparation, composition formulation and composition use are described in detail as follows. All concentrations and ratios are expressed on a weight basis unless otherwise indicated.

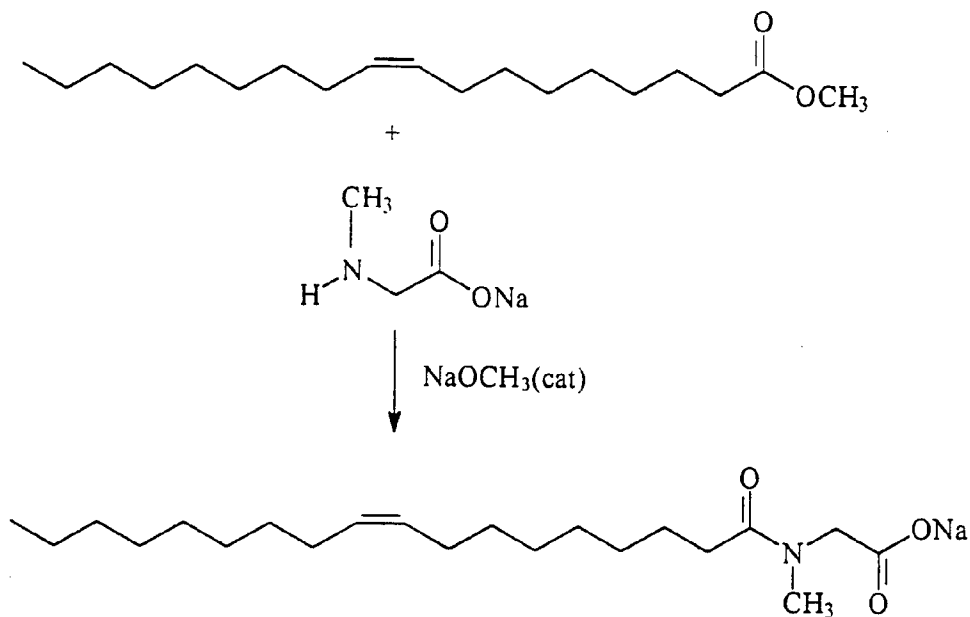
(A) The Oleoyl Sarcosinate-Containing Surfactant Component

The detergent compositions herein essentially contain at least about 1% of a deterative surfactant component which comprises oleoyl sarcosinate. Preferably the oleoyl sarcosinate will comprise from about 0.1% to about 80%, more preferably from about 1% to about 40%, and most preferably about 2% to about 30% by weight of the compositions. Oleoyl sarcosinate is an anionic surfactant which may be utilized in its acid and/or salt form. Oleoyl sarcosinate has the general formula: $C_{17}H_{33}C(O)N(CH_3)CH_2COOM$ wherein M is hydrogen or cationic moiety. The configuration of oleoyl sarcosinates can be represented as follows:



Preferred M substituents are hydrogen and alkali metal cations, especially sodium and potassium. Oleoyl sarcosinate is commercially available, for example as Hamposyl O marketed by W. R. Grace & Co.

15 In addition to the commercially-available oleoyl sarcosinate, oleoyl sarcosinate useful herein can also be prepared from the ester (preferably the methyl ester) or oleic acid and a sarcosine salt (preferably the sodium salt) under anhydrous reaction conditions in the presence of a base catalyst with a basicity equal to or greater than alkoxide catalyst (preferably sodium methoxide). For example, the reaction may illustrated by the scheme:



This salt may be optionally neutralized to form the oleoyl sarcosinate in its acid form.

The preferred method for preparing oleoyl sarcosinate is conducted at a temperature from about 80°C to about 200°C, especially from about 120°C to about 200°C. It is preferred to conduct the reaction without solvent although alcohol solvents which have a boiling point of at least 100°C and are stable to the reaction conditions (i.e., glycerol is not acceptable) can be used. The reaction may proceed in about 85% yield with a molar ratio of methyl ester reactant to sarcosine salt reactant to basic catalyst of about 1:1:0.05-0.2.

Methyl ester mixtures derived from high oleic content natural oils (preferably having at least about 60%, more preferably at least about 75%, and most preferably at least about 90% oleic content) are especially preferred as starting materials. Examples include high-oleic sunflower and rapeseed/canola oil. In addition, a high-oleic methyl ester fraction derived from either palm kernel oil or tallow is acceptable. It is to be understood that such oils typically will contain some levels of impurities, including some fatty acid impurities that may be converted to sarcosinate compounds by this synthesis method. For example, commodity canola/rapeseed oil may comprise a majority of oleic acid, and a mixture of fatty acid impurities such as palmitic, stearic, linoleic, linolenic and/or eicosenoic acid, some or all of which are converted to the sarcosinate by this reaction method. If desired for formulation purposes, some or all of such impurity materials may be excluded from the starting oil before preparing the oleoyl sarcosinate to be used in the present invention.

Finally, sarcosine remaining in the reaction mixture can be converted to an amide by addition of maleic or acetic anhydride to the mixture, thereby minimizing the sarcosine content and any potential for formation of undesired nitrogen-containing impurities.

The synthesis of oleoyl sarcosinate may be carried out as follows to prepare the sodium oleoyl sarcosinate.

Synthesis of Oleoyl Amide of Sarcosine Sodium Salt - A 2 L, 3-neck round bottom flask is fitted with thermometer, Dean-Stark trap with condenser, mechanical stirring, and a gas inlet adapter through which nitrogen is passed over the reaction mixture. The reaction vessel is charged with sarcosine (43.3 g, 0.476 mol), sodium methoxide 25% in methanol (97.7 g, 0.452 mol), and methanol (400 mL). The reaction mixture is refluxed 15 min. to neutralize the sarcosine and then methyl ester derived from Cargill regular high-oleyl sunflower oil (148.25 g, 0.5 mol) is added. After the methanol is removed with the Dean-Stark trap, reaction mixture is heated to 170°C for 1 hr. to drive off any water. The reaction is initiated by the addition of

sodium methoxide 25% in methanol (15.4 g, 0.0714 mol). The reaction mixture is kept at 170°C for 2.5 hr. during which methanol is collected in the Dean-Stark trap. The reaction is allowed to cool slightly, and then methanol (200 g) is added. Maleic anhydride (9.43 g, 0.095 mol) is added to the methanol solution, and the reaction is stirred at 60°C for 0.5 hr. Then most of the methanol is removed by rotary evaporation, and acetone (2 L) is added to precipitate the product. The product is collected by suction filtration and allowed to air dry to give an off-white solid. Analysis of the reaction mixture by GC indicates the majority of the product is oleoyl sarcosinate, with minor amounts of the following impurities: sarcosine, oleic acid, and the sarcosinates derived from palmitic acid, stearic acid, and linoleic acid.

The deterative surfactant component of the compositions herein may optionally, and preferably will, also comprise one or more additional non-sarcosinate deterative surfactants. Optional deterative surfactants utilized can be of the anionic, nonionic, cationic, zwitterionic, or ampholytic type or can comprise compatible mixtures of these surfactant types. Optional deterative surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972; U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975; U.S. Patent 4,222,905, Cockrell, issued September 16, 1980; in U.S. Patent 4,239,659, Murphy, issued December 16, 1980; in U.S. Patent 4,259,217, Murphy, issued March 31, 1981; and in U.S. Patent 4,260,259, Letton, issued April 7, 1981. All of these patents are incorporated herein by reference.

Of these optional surfactants, anionics and nonionics are preferred and non-sarcosinate anionics are most preferred. Such preferred optional anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium salts, and the ammonium, alkylammonium and alkanolamine salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Soaps can also perform a builder function in the detergent compositions herein. Use of fatty acid soaps in the compositions herein will generally result in a diminution of sudsing. This effect should be taken into account by the formulator.

Additional non-sarcosinate anionic surfactants which suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium,

alkylammonium and alkanolamine salts, or organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic

5 surfactants are a) the sodium, potassium and ethanolamine alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ethanolamine alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and

10 wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in

15 which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁₋₁₃ LAS.

Preferred optional nonionic surfactants are those of the formula R¹(OC₂H₄)_nOH, wherein R¹ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products

20 of C₁₂-C₁₅ alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C₁₂-C₁₃ alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula



wherein R is a C₉₋₁₇ alkyl or alkenyl, R₁ is a preferably a methyl or 3-methoxypropyl group and Z is glycyl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide and other C₁₂-C₁₈ N-methylglucamides. See

30 WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures

35 of which are incorporated herein by reference.

Preferably, the detergent compositions herein will comprise from about 5% to 60% of the deterative surfactant component. More preferably, such compositions will comprise from about 10% to 45% of a deterative surfactant. If optional non-sarcosinate surfactants are employed, these optional surfactants will generally
5 comprise from about 30% to 95%, more preferably from about 50% to 85%, of the deterative surfactant component of the compositions herein.

(B) Calcium and/or Magnesium Ions

The detergent compositions herein also essentially comprise at least 0.05% of a
10 water-soluble source of calcium ions, magnesium ions, or mixtures of calcium and magnesium ions. Typical detergent compositions herein, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium and/or magnesium ion per liter of finished composition. The
15 compositions preferably are formulated such that the deterative wash liquor contains from about 0.01 to about 0.5 mmole/liter of magnesium and/or calcium ions, more preferably from about 0.03 to about 0.2 mmole/liter.

Any water-soluble calcium salt can be used as the source of calcium ion including, but not limited to, calcium chloride, calcium sulfate, calcium malate,
20 calcium hydroxide, calcium formate and calcium acetate. A small amount of calcium ion, generally from about 0.05 to about 0.04 millimoles per liter, is often also present in the composition due to calcium in the slurry for any enzyme which may be present and/or in formula water. In solid detergent compositions the formulation may include a sufficient quantity of water-soluble calcium ion source to provide such
25 amounts in the washing liquor. In the alternative, natural water hardness may suffice.

Instead of or in addition to the calcium ion source, the compositions herein can also contain a water-soluble source of magnesium ions. Suitable and convenient Mg^{++} sources include, but are not limited to: $Mg(OH)_2$, $MgCl_2$, $MgSO_4$, and the formate, citrate, malate and maleate salts of magnesium as well as mixtures of these
30 magnesium ion sources.

As with calcium ions, incorporation of magnesium cations in the detergent compositions of this invention can enhance cleaning performance, especially with regard to greasy soils of the type typically encountered in dishwashing operations. However, addition of magnesium cations can create special problems in the instance
35 wherein the detergent compositions herein are in the form of aqueous gels. This is because the presence of ionic ingredients, e.g., Mg^{++} , in such products does tend to decrease gel viscosity. For lower viscosity gels herein (500,000-1,500,000 cps) the

addition of common magnesium salts such as magnesium chloride, magnesium sulfate, magnesium formate, magnesium citrate, and the like can also be used to selectively control final product viscosity. For gels of higher viscosity (above about 2,000,000 cps), such magnesium salts can disrupt the desired physical properties and such common magnesium salts are preferably not used above about 0.3% levels. In order to overcome this problem and to allow the formulator to incorporate magnesium cations at levels of about 0.5% and greater, generally up to about 2%, typically 0.5%-1.5%, in the finished gels, it is preferred to add at least some of the magnesium in the form of the magnesium salt of the anionic surfactant. Stated otherwise, all of the magnesium cations can be added as the magnesium form of the surfactant, or part can come from the magnesium surfactant and part from other magnesium salts as noted above. The magnesium form of the alkyl alkoxy sulfate surfactant can be generated *in situ* by combining $Mg(OH)_2$ with the acid form of the surfactant during the mixing step of composition formation. In an alternate mode, the use of other surfactants such as the C_{16} dimethyl amine oxides, C_{12} - C_{14} amine oxides, and/or C_{12-14} betaine surfactants will assist in the formulation of magnesium-containing gels.

Giving the foregoing considerations, a source of calcium and/or magnesium ions can be used in the compositions herein in amounts which are sufficient to provide calcium and/or magnesium ions in washing solution in concentrations that provide an enhanced measure of grease/oil removal properties to the sarcosinate-containing detergent compositions of this invention. Preferably, the water-soluble source of calcium and/or magnesium ions will comprise from about 0.05% to 2.0% of the detergent compositions herein, more preferably from about 0.2% to 1.5%, of the detergent compositions herein. When mixtures of calcium and magnesium ions are to be utilized, ratios of Mg:Ca of from about 1:0 to 1:5 will generally be used.

(C) Optional Detergent Composition Components

In addition to the oleoyl sarcosinate-containing surfactant composition and the calcium/magnesium source essentially utilized, the detergent compositions herein may also comprise a wide variety of optional ingredients. Such optional ingredients include detergent builders, enzymes, liquid carriers and solvents, and other conventional detergent composition adjuvants.

35 a) Detergent Builder

The detergent compositions herein may also optionally comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions

in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium, and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO₂ to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also, crystalline layered silicates such as those discussed in Corkill et al., U.S. Patent No. 4,605,509, incorporated herein by reference, are suitable for use in the detergent composition of the invention.

b). Enzymes

While not essential to the detergent compositions of this invention, it is preferable to include an enzyme component. Suitable enzyme components are available from a wide variety of commercial sources. For example, suitable enzymes are available from NOVO Industries under product names T-Granulate™ and Savinase™, and Gist-Brocades under product names Maxacal™ and Maxatase™. Included within the group of enzymes are proteases, amylases, lipases, cellulases and

mixtures thereof. The enzyme concentration preferably should be from about 0% to about 5%, more preferably from about 0.001% to about 2.5%, and most preferably from about 0.01% to about 2%. Typically, proteases are used at an Activity Unit (Anson Unit) level of from about 0.001 to about 0.05, most preferably from about 0.002 to about 0.02, while amylases are used at an amylase unit level of from about 5 to about 5000, most preferably from about 50 to about 500 per gram of detergent composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Most preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus*, particularly *Bacillus lentus*, in which arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4; U.S. Patent No. 5,185,250; and U.S. Patent No. 5,204,015. Also preferred are protease which are described in copending application U.S. Serial No. 08/136,797, entitled Protease-containing Cleaning Compositions and copending Application U.S. Serial No. 08/136,626, entitled Bleaching Compositions Comprising Protease Enzymes, which are incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

c). Conventional Detergent Composition Ingredients

The detergent compositions of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzyme-stabilizing agents, hydrotropes, carrier liquids, and perfumes. (See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., the disclosure of which is incorporated herein by reference.) Dye transfer inhibiting agents and optical brighteners may also be included.

Chelating agents are described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54, through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976, to Bartoletta et al., and 4,136,045, issued January 23, 1979, to Gault et al., both incorporated herein by reference. Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al., issued August 9, 1988, column 6, line 3 through Column 7, line 24, incorporated herein by reference. A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

Optional components such as alkalinity sources, pH adjusting agents, clay and carrier liquids can comprise a substantial amount, e.g. up to about 80%, of the detergent compositions herein. Other conventional optional detergent composition adjavents comprise much smaller amounts of the compositions, i.e. up to about 10% of the compositions.

(d) Bleaching Compounds - Bleaching Agents and Bleach Activators -

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now

known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction
 5 encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application
 10 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy-caproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

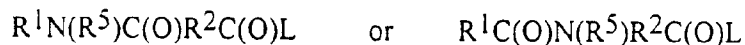
15 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

20 A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with
 25 silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in
 30 aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See
 35 also U.S. 4,634,551 for other typical bleaches and activators useful herein.

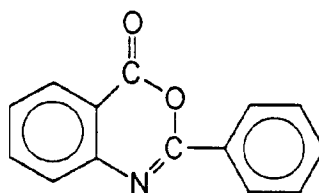
Highly preferred amido-derived bleach activators are those of the formulae:



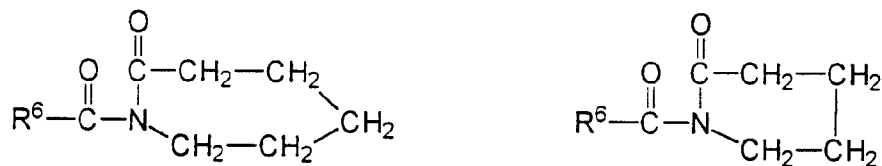
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or

aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

- 5 If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of
- 10 these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures
- 15 thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.
- 20 As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

25

(D) Detergent Composition Formulation

The detergent compositions according to the present invention can be in liquid, gel or granular forms. Such compositions can be prepared by combining the essential

30 and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients (e.g. surfactants, builders, water, etc.) as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The

35 remaining dry ingredients can be admixed in granular powder form with the spray dried granules in a rotary mixing drum and the liquid ingredients (e.g. enzymes, binders and perfumes) can be sprayed onto the resulting granules to form the finished

detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. greater than about 600 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular
5 detergents; typical filler salts are alkali earth metal salts of sulfates and chlorides, typically sodium sulfate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing
10 components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form." In such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

In general, detergent compositions herein in gel form can also be prepared by
15 admixing essential and optional ingredients together in the required amounts. However, the formulation of gels is a complex phenomenon involving the association of solute molecules in an aqueous medium. While a precise definition of the gel state is difficult, most aqueous gels can be considered as having most of the properties of a solid or semi-solid, while still containing as high as 99% water. Gels of the type used
20 as the gel detergent compositions provided herein are typically in the form of gelatinized or gelled compositions which can have viscosities as high as 5,000,000 centipoise, and typically range from about 500,000 to about 4,000,000 centipoise. A wide variety of means have been used to form gels, and standard formularies reveal that various commercial gums are used for this purpose in various consumer
25 products. For example, see M.G. deNavarre "The Chemistry and Manufacture of Cosmetics" Vol. III 2nd ed. 1975 Continental Press, Orlando, Florida USA. Materials such as urea and urea derivatives can also be used to form gels.

The compositions of the present invention are formulated so as to have a pH of at least about 6.5, preferably greater than about 7, in the washing solution at
30 conventional usage concentrations in order to optimize cleaning performance on greasy and oily soils; acidic wash solution pH's tend to decrease performance on such soils. Preferably, the compositions herein are more alkaline in nature when placed in the washing solution and have a pH of greater than about 7.5. Some of the sarcosinate/calcium/magnesium systems of the present invention will attain optimum
35 removal of greasy/oily soils at these higher pH's. In such systems, overall performance may be improved by varying the wash solution pH during the washing

process. Composition and washing solution pH will generally be no greater than about 11, preferably no greater than about 10.5.

(E) Fabric Laundering, Dishwashing and Pretreatment Methods

5 The present invention also provides a method for laundering fabrics or washing dishes soiled with greasy/oily stains or soil. Such a method employs contacting these fabrics or dishware with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described. Contacting of fabrics or dishware with washing solution will generally occur under conditions of agitation.

10 For fabric laundering, agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabrics in a conventional clothes dryer. For dishwashing, agitation can be carried out in a conventional automatic dishwashing machine. For use of light duty liquids to clean dishes, agitation of the washing solution is generally carried out by hand. Dishware
15 surfaces are usually cleaned by a hand-held apparatus such as a rag, sponge, or brush.

 An effective amount of the liquid, granular or gel detergent compositions in the aqueous wash solution in the washing machine, automatic dishwasher, or hand dishwashing solution, is preferably from about 500 to about 10000 ppm. More preferably from about 1000 to 3000 ppm of the detergent compositions herein will be
20 provided in aqueous washing solutions.

 The detergent compositions herein may also be used to pretreat substrates containing greasy/oily soils or stains prior to washing such substrates using conventional aqueous washing solutions. Such pretreatment involves the application of highly concentrated forms of the detergent compositions herein directly onto the
25 greasy or oily stains or soils found on the substrate to be cleaned. For compositions herein in liquid or gel form, this will generally involve the direct application of the composition as is to the stain/soil on the substrate. For detergent compositions herein in granular form, pretreatment involves the application of an aqueous paste formed from such granular products. Aqueous pastes of this type will generally
30 contain from about 1% to 50% water, preferably from about 5% to 20% water.

 Pretreatment of greasy/oily stains or soils will generally occur for a period of from about 30 seconds to 24 hours prior to washing the pretreated soiled/stained substrate in conventional manner. More preferably, pretreatment times will range from about 1 to 180 minutes.

35

EXAMPLES

The following examples illustrate the compositions of the present invention but are not necessarily meant to limit or otherwise define the scope of the invention.

5

EXAMPLE I

Several heavy duty liquid laundry detergent compositions are prepared. The formulation for these compositions are set forth in Table I.

TABLE I
Heavy Duty Liquid Detergent Compositions

	Component	Wt. %			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
10	Oleoyl sarcosinate	10.0	9.0	3.0	10.0
	Calcium chloride	0.9	---	0.3	0.2
	Magnesium chloride	---	1.2	0.6	---
15	Magnesium sulfate	---	---	0.9	---
	C ₁₂ -C ₁₅ Alkyl ethoxylated sulfate	13.0	14.0	14.0	15.0
	C ₁₂ -C ₁₄ N-methyl glucamide	6.0	6.0	6.0	6.0
	C ₁₂ -C ₁₄ Fatty alcohol ethoxylate	3.0	3.0	3.0	3.0
	C ₁₂ -C ₁₆ Fatty acid	9.0	6.8	14.0	14.0
20	Citric acid anhydrous	6.0	4.5	3.5	3.5
	Diethylene triamine penta acetic acid (DTPP)	1.0	1.0	2.0	2.0
	Monoethanolamine	13.2	12.7	12.8	11.0
	Propanediol	12.7	14.5	13.1	10.0
25	Ethanol	1.8	1.8	4.7	5.4
	Enzymes (protease, lipase, cellulase)	2.4	2.4	2.0	2.0
	Terephthalate-based polymer	0.5	0.5	0.5	0.5
	Boric acid	2.4	2.4	2.8	2.8
	2-butyl-octanol	2.0	2.0	2.0	2.0
30	(1)DC 3421 R	0.3	0.4	0.3	0.4
	(2)FF 400 R				
	Tinopal UNPA-GX Brightener	0.075	0.21	---	---
	Tinopal 5BM-GX Brightener	---	---	0.21	0.075
	Water & minors	-----up to 100%-----			

35

(1)DC 3421 is a silicone oil commercially available from Dow Corning.

(2)Is a silicone glycol emulsifier available from Dow Corning.

The compositions described in Table I are suitable for laundering fabrics soiled with grease or oil using aqueous washing solutions formed from such compositions. The compositions in Table I are also especially effective for pretreating fabrics with greasy or oily stains. To effect such pretreatment, greasy stains and soils on the fabrics are contacted with the full strength Table I liquid compositions for 30 minutes prior to washing the fabrics in a conventional fabric laundering process.

EXAMPLE II

Several compact granular laundry detergent compositions are prepared. The formulations for these compositions are set forth in Table II.

TABLE II
Granular Detergent Compositions

Component	Wt. %		
	A	B	C
Oleoyl sarcosinate	5.8	6.1	10.2
Calcium chloride	1.3	---	0.4
Magnesium chloride	---	1.2	0.6
C ₁₁ -C ₁₄ Linear alkyl benzene sulfonate	6.17	---	---
C ₁₂ -C ₁₅ Alkyl alkoxylated sulfate	---	4.0	---
C ₁₂ -C ₁₄ N-methyl glucamide	---	---	1.0
C ₄₅ alkyl sulfate	3.00	3.00	3.00
C ₄₅ alcohol 7 times ethoxylated	4.00	4.00	4.00
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50
Maleic acid acrylic acid copolymer	5.00	5.00	5.00
Cellulase (active protein)	0.03	0.03	0.03
Alkalase/BAN	0.60	0.60	0.60
Lipase	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00
Sodium sulfate	3.50	3.50	3.50
Brightener	0.20	0.20	0.20
Water & minors	-----Balance to 100%-----		

The compositions described in Table II are suitable for laundering fabrics soiled with grease or oil using aqueous washing solutions formed from such compositions.

5

EXAMPLE III

Several light duty liquid dishwashing detergent compositions of the present invention are described in Table III.

10

TABLE III
Light Duty Dishwashing Liquids

<u>Component</u>	<u>% By Weight</u>				
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
C ₁₂ -C ₁₄ Alkyl ethoxy sulfate (1 EO)	16	9	12	--	16
C ₁₂ -C ₁₄ Alkyl ethoxy sulfate (3 EO)	--	14	--	11	--
15 C ₁₀ Alkyl ethoxylate (8 EO)	7	3	7	1	8
C ₁₂ -C ₁₄ N-methyl glucamide	8	9	12	6	8
Coconut diethanolamide	--	--	--	5	--
Dimethyl dodecyl amine oxide	--	1	--	2	--
Oleoyl sarcosinate	2	1	3	2	2
20 Magnesium chloride	--	--	1	1	0.7
Calcium chloride	0.5	1	--	--	0.3
Sodium toluene sulfonate	3	3	3	3	2*
Ethanol	4	4	4	4	4.5
Water	-----Balance-----				
25 *Sodium cumene sulfonate					

The compositions of Table III are suitable for washing dishware soiled with grease or oil using aqueous washing solutions formed from such compositions.

30

EXAMPLE IV

A granular automatic dishwashing detergent of the present invention is shown in Table IV.

<u>Component</u>	<u>Wt. %</u>
Oleoyl sarcosinate	3.0
35 Sodium citrate	15.0
Sodium carbonate	15.0
Nonionic suds suppressor (1)	4.0

	Sodium polyacrylate	4.0
	Sodium silicate solids ($\text{SiO}_2:\text{Na}_2\text{O}$, 2.0 ratio)	6.6
	Chlorine bleach solids (2)	1.9
	Sodium $\text{C}_{12/13}$ alkyl ethoxy (3.0 ave.) sulfate	2.0
5	C_{12-18} N-methyl glucamide	4.0
	Calcium sulfate dihydrate	2.5
	Sodium sulfate, perfume, dye and water	Balance
	(1) Blend of ethoxylated monohydroxy alcohol and polyoxyethylene/ polyoxypropylene block polymer. Includes 3.2% monstearyl acid phosphate for suds suppression.	
10		
	(2) Sodium dichloroisocyanurate dihydrate.	

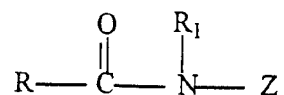
The composition of Table IV is suitable for cleaning dishware soiled with grease and/or oil when such a composition is utilized in a conventional automatic dishwashing machine.

WHAT IS CLAIMED IS:

Claims:

1. A detergent composition especially useful for removing greasy/oily stains from substrates during washing or cleaning operations, which composition comprises:
 - (a) at least 1% by weight of a deterative surfactant component comprising an oleoyl sarcosinate surfactant of the formula:
$$\text{C}_{17}\text{H}_{33}\text{C}(\text{O})\text{N}(\text{CH}_3)\text{CH}_2\text{COOM}$$
wherein M is H or a cationic moiety; and
 - (b) at least 0.05% by weight of a water-soluble source of calcium ions, magnesium ions or mixtures of calcium and magnesium ions.
2. A composition according to Claim 1 wherein
 - (a) in the formula for the oleoyl sarcosinate, M is selected from sodium and potassium; and
 - (b) the source of calcium and magnesium ions is selected from sulfate, chloride, formate, malate, acetate, citrate, maleate and anionic surfactant salts of calcium and magnesium.
3. A composition according to either of Claims 1 or 2 wherein
 - (a) the deterative surfactant component comprises from 5% to 60% of the composition; and
 - (b) the calcium and magnesium source comprises from 0.1% to 2.0% of the composition.
4. A composition according to any of Claims 1-3 wherein the deterative surfactant component comprises from 30% to 95% of the deterative surfactant component of a non-sarcosinate surfactant selected from anionic, nonionic, cationic, zwitterionic, and ampholytic surfactants and mixtures of these surfactant types.
5. A composition according to Claim 4 wherein the non-sarcosinate surfactant is selected from:
 - (a) sodium and potassium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;
 - (b) sodium and potassium C₉ to C₁₅ alkyl benzene sulfonates;
 - (c) sodium and potassium C₈ to C₁₈ alkyl sulfates;
 - (d) nonionic surfactants of the formula $\text{R}^1(\text{OC}_2\text{H}_4)_n\text{OH}$ wherein R^1 is a C₁₀ - C₁₆ alkyl group or a C₈ - C₁₂ alkylphenyl group and n is from 3 to 80;

- (e) polyhydroxy fatty acid amides of the formula



wherein R is C₉₋₁₇ alkyl or alkenyl, R₁ is methyl or 3-methoxypropyl group and Z is glyceryl derived from a reduced sugar or alkoxyated derivatives thereof; and

- (f) combinations of these non-sarcosinate surfactants.
6. A composition according to any of Claims 1-5 wherein the water-soluble source of calcium and magnesium ions is selected from calcium chloride, calcium sulfate, magnesium chloride, magnesium sulfate and combinations of these salts.
 7. A composition according to any of Claims 1-6 which contains sources of both calcium and magnesium ions in an Mg:Ca ratio of from 1:0 to 1:5.
 8. A composition according to any of Claims 1-7 which additionally comprises from 0.1% to 80% of a detergent builder.
 9. A composition according to Claim 8 which additionally contains from 1% to 70% by weight of a detergent builder selected from sodium carbonate, sodium silicate, crystalline layered silicates, aluminosilicates, oxydisuccinates and citrates.
 10. A composition according to any of Claims 1-9 which additionally contains from 0.001% to 5.5% of an enzyme component selected from proteases, amylases, lipases, cellulases, and mixtures of such enzyme types.
 11. A composition according to any of Claims 1-10 which additionally contains up to 80% of the composition of one or more detergent composition adjuvants selected from suds boosters, suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, germicides, pH adjustment agents, non-builder alkalinity sources, chelating agents, smectite clays, enzyme-stabilizing agents, hydrotrope, carrier liquids, perfumes, optical brighteners and dye transfer inhibition agents.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/06298

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,93 05132 (THE PROCTER & GAMBLE CO.) 18 March 1993 cited in the application see page 4 - page 7 see page 23 - page 24 see claims ---	1-9,11
A	US,A,5 030 378 (VENEGAS M.G.) 9 July 1991 cited in the application see the whole document ---	1,2,4-6, 8-11
A	EP,A,0 576 778 (THE PROCTER & GAMBLE CO.) 5 January 1994 see the whole document ---	1,4,5, 8-11
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/06298

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 95/06298

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		EP-A- 0602179	22-06-94
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		HU-A- 68189	29-05-95
		JP-T- 6510326	17-11-94
		NO-A- 940759	06-05-94
		NZ-A- 244226	28-08-95
		PT-A- 100841	28-02-94

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		EP-A- 0229690	22-07-87

GB-A-459039		NONE	
